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**GROWTH AND CHARACTERIZATION OF CRYSTALS FOR IR
DETECTORS AND SECOND HARMONIC GENERATION DEVICES***

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ABSTRACT

Two types of materials, L-Arginine Phosphate (LAP) and doped Triglycine Sulfate (TGS), are examined for their growth characteristics and relevant properties for second harmonic generation and IR detector applications respectively.

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GROWTH AND CHARACTERIZATION OF CRYSTALS FOR IR DETECTORS AND SECOND HARMONIC GENERATION DEVICES

A. L-Arginine Phosphate Crystals

Introduction

LAP is considered to be a potential new material for efficient second harmonic generation for an Nd:YAG laser. It is phase matchable with conversion efficiency between 3 to 4 times that of potassium dihydrogen phosphates (KDP). It has a high damage threshold (about 50 times of KDP) and a high figure of merit (40 times of KDP). Being a fairly new material, little data are available in the literature on growth parameters under which optical quality crystal can be grown from solution. In this section, characteristics of LAP solution and growth kinetics of LAP crystals grown under different conditions are described. The preliminary results of second harmonic conversion efficiency of LAP Crystals in comparison with KDP are also discussed.

Experimental Procedures and Results

The compound L-arginine phosphate, which is not commercially available, was synthesized in the laboratory. L-arginine and phosphoric acid were mixed in stoichiometric ratio and dissolved in deionized water. The mixture was stirred and heated to dissolve homogeneously. The chemical reaction can be presented as $C_6H_{14}N_4O_2 + H_3PO_4 \rightarrow C_6H_{16}N_4O_3 \cdot H_3PO_4$. The solution was kept at room temperature for evaporation. The self nucleated crystallites of LAP compound were formed and were removed from solution and dried. In order to find that the compound was in fact LAP, a powder sample was prepared and packed into a thin cell formed by two glass slides. The sample was illuminated with a 1064nm Nd:YAG laser and the second harmonic output from the sample which was green in color, was observed (corresponding to 532 nm wave length). This confirmed the formation of an L-arginine phosphate compound. Since no data were available about the solubility of LAP in water, it was determined at various temperatures. The details of the method are described elsewhere (1). The solubility data for LAP compound are presented in Table I.

Table I
Data for Solubility of LAP in Water

S.No.	Temperature (°C)	Solubility (gm/100 gm of Water)
1	28.0	13.93
2	35.0	20.04
3	40.0	25.66
4	45.0	32.32
5	50.0	40.02

The index of refraction of a solution is a sensitive indicator of the concentration. The measurements of the refractive index of LAP solution were made using an Abbe refractometer with a temperature controlled sample stage, and white light. Fig. 1. shows the index of refraction of the saturated solution as a function of temperature. The growth of crystals from the solution depends on various parameters: temperature of growth, degree of supersaturation, character of solution and hydrodynamic conditions. In the present work, in order to find the optimum conditions under which optical quality crystals can be grown, character of solution (pH) and hydrodynamics conditions were varied, keeping other conditions constant. The crystals were grown using temperature lowering techniques in a modified crystallizer (1,2). It was found that the morphology and optical quality of the LAP crystal changes with the pH of the solution. The optical quality crystals with prismatic morphology were grown from solution with optimum pH. At the optimum value of the pH of the solution, it was found that rotating the seeds between 17-26 rpm does not affect significantly the morphology and optical quality of the crystals. Single crystals of LAP, cut and polished, were placed in an Nd:YAG laser beam (1064nm) and the second harmonic was recorded at 532.2nm. The conversion efficiency of LAP samples was comparable with that of KDP. The lower value may be due to small thickness and bad polish. Further work to understand the growth mechanism and optical studies are in progress. The most important task, reducing growth time and increasing the growth rate in the desired direction, is also in progress.

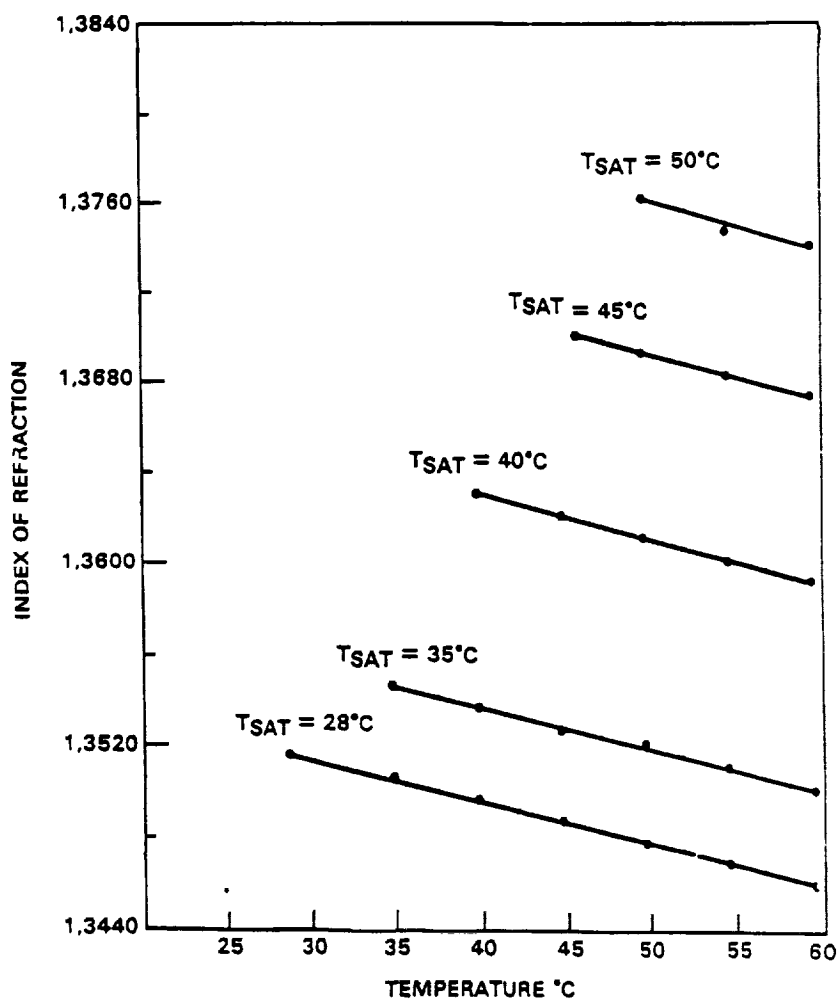


Figure 1. Index of Refraction Versus Temperature for LAP Solution.

B. Triglycine Sulfate Crystals

Introduction

TGS is a well known ferroelectric material and is widely used for i.r. detection at room temperature in scientific, medical, and commercial applications. It is the most sensitive material among available pyroelectric materials. However, it has a strong tendency of depoling ($T_c = 49^\circ \text{C}$) due to temperature and mechanical shocks, causing degradation of the detector performance. In order to improve the pyroelectric properties and check depoling, various dopants have been tried. In this section, growth and characteristics of doped TGS crystals are described. The results are compared with a pure TGS crystal.

Experimental Procedure and Results

Triglycine sulfate crystals were grown using the reciprocating crystallizer designed and fabricated in the workshop of the Physics Department (2,3). The seed crystals with the desired amount of dopants were grown by slow evaporation. The detail of the method of growing crystals, growth kinetics and characterization techniques for electrical and detector properties are described elsewhere (3,4). The detectors were fabricated and tested at EDO Corporation / Barnes Engn. Div., Shelton, CT. The results of measurement for material characteristics are presented in Table II. It can be inferred from the table that the figure of merit of TGS crystals doped with L-alanine and simultaneously doped with L-alanine and cesium is higher than that of the pure TGS crystal. Moreover, L-AL+Cs doped TGS crystals are relatively harder and easier for sample handling and processing. The detector characteristics of doped TGS crystals are presented in Table III. It is shown that Detectivity (D^*) of L-alanine doped crystals is higher than for other crystals investigated. It is probably the best value reported so far in the literature. The amount of dopant and conditions of growth chosen resulted in uniform incorporation of L-alanine in the crystal, as can be seen from the values of D^* obtained for five detectors fabricated on one chip.

Conclusion

The present studies demonstrate that large optical quality LAP crystals can be grown by a solution cooling technique in a reciprocating crystallizer. However, studies to understand the role of the character of the solution (pH and dopants) on the crystal growth and optical quality of LAP crystals are required.

From the work on TGS crystals, it can be concluded that L-alanine and Cs+L-alanine doped crystals are attractive for pyroelectric infrared detector applications.

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TABLE II
MATERIAL PARAMETERS OF TGS CRYSTALS

CRYSTAL	PYROELECTRIC COEFFICIENT, p (nc/cm ² °C)				DIELECTRIC CONSTANT ϵ'				FIGURE OF MERIT p/ϵ' (nc/cm ² °C)			
TEMP °C	30	35	40	45	30	35	40	45	30	35	40	45
TGS	53	70	98	170	48	64	106	250	1.1	1.09	0.92	0.68
TGS + Ce	37.2	53	84	150	61	76	115	350	0.61	0.7	0.73	0.42
TGS + Cs	43	64	85	155	67	84	120	300	0.64	0.76	0.70	0.52
TGS + LA	38	44	80	172	30	37	48	62	1.2	1.48	1.6	2.7
TGS + Cs + LA	55	134	200	315	38	41	54	69	1.44	3.26	3.7	4.5

TABLE III
DETECTOR CHARACTERISTICS

SAMPLE	CELL NO.	RESPONSIVITY (V/W) 1000 K/BLACKBODY		NOISE (nV/Hz)		D^* (1000K,f,1) x10 ⁸	
		15 Hz	90 Hz	15 Hz	90 Hz	15 Hz	90 Hz
NO. 1 (TGS)	20930	1 x 10 ³	160	260	80	7.7	4.0
	20944	1 x 10 ³	160	170.5	56	12.0	5.5
NO. 2 (TGS + L-ALANINE)	20752	1 x 10 ³	160	190	65	11.0	5.0
	20885	1 x 10 ³	160	167	60	11.8	5.3
	20963	950	160	190	66	12.0	5.2
	20803	1 x 10 ³	160	175	60	13.5	5.6
	20941	1 x 10 ³	160	167	54	12.3	5.7
NO. 3 (TGS + Cs + L-ALANINE)	20986	1 x 10 ³	150	560	140	3.35	2.05
	20924	850	130	280	92.5	6.25	3.0
	20980	890	140	760	170.5	2.20	1.6

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